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COMPUTATIONAL STUDY OF QUINAZOLINONE DERIVATIVES USING DENSITY FUNCTIONAL THEORY CALCULATIONS

N. Prabavathi* & A. Nilufer**
* Department of Physics, Sri Sarada College for women (Autonomous), Salem, Tamilnadu
** Department of Physics, Gnanamani College of Technology, Paachal, Namakkal, Tamilnadu

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Abstract:

The DFT calculations were performed with the Gaussian 09 package on the quinazolinone derivatives such as 2-methyl-4(3H)quinazolinone (MHQ) and 2-trichloromethyl-4(3H)-quinazolinone (TCMQ). This study gives a complete description of the molecular geometry and molecular vibrations of the titled molecules. In addition to that, the NMR, UV-VIS, total static first hyperpolarizability, HOMO-LUMO,NBO and charge analysis were carried out to get an insight into the electronic properties of the chosen molecules.

Key Words: DFT, Computational Chemistry, Gaussian 09, Natural Bond Orbitals & HOMO- LUMO

1. Introduction:

Gaussian 09 is a computational chemistry program that runs on any modern Windows 32-bit PC. With Gaussian 09, one can thoroughly investigate the chemical problems. A modern DFT calculation can be done using a quantum chemical code. A basis set is chosen, which assigns predetermined functions to describe the electrons on each atom of the molecule being studied. Finally, a DFT approximation called the exchange-correlation energy is chosen, and the code starts running. For each guess of the nuclear positions, the code calculates an approximate energy. A geometry optimization should find the minimum energy configuration. With variations on this theme, one can read out the molecular geometries, dissociation energies, reaction barriers, vibrational frequencies, etc. Density functional theory (DFT) of electronic structure has made an unparalleled impact on the application of quantum mechanics to interesting and challenging problems in chemistry. DFT would correctly describe the quantum nature of matter. The computational approach of DFT using Gaussian 09 software is to find the three-dimensional density. The DFT calculations are carried out using B3LYP which is the most widely used of all the functionals. Gaussian 09 can predict a variety of spectra including IR and Raman, NMR, UV/Visible. However, observed spectra are often difficult to interpret. The results of electronic structure calculations can be vital to this process. This combination of experimental observation and theoretical computation can yield very accurate structural and spectral data for compounds of interest. Interestingly, the quinazolinone derivatives such as 2-methyl-4(3H)quinazolinone (MHQ) and 2-trichloromethyl-4(3H)-quinazolinone (TCMQ) were chosen due to their enormous applications in various fields

2. Computational Details:

The quantum chemical calculation of 2-methyl-4(3H)quinazolinone (MHQ) and 2-trichloromethyl-4(3H)-quinazolinone (TCMQ) has been performed using the B3LYP level of theory supplemented with the standard 6-311++G** basis set, using the Gaussian 09 program [1]. In all computations, no constraints were imposed on the geometry. Full geometry optimization was performed until a stationary point for the local minimum was found. Normal coordinate analysis on TCMQ and MHQ has been performed to obtain full description of the molecular motion pertaining to the normal modes using the MOLVIB program [2, 3]. By combining the results of the Gauss view program [4] with symmetry considerations, vibrational frequency assignments are made with a high degree of confidence.

3. Results and Discussion:

3.1 Molecular Geometry: At the optimized structure of the molecule no imaginary frequency modes were obtained, which confirms that a true minimum on the potential energy surface was found. The optimized geometry of the chosen molecules is presented in Figure 1. As the ring carbon atoms exerts a large attraction on valence electron cloud of nitrogen atom, the C–N bond lengths vary within the range 1.28 – 1.40 Å. The C4–C5 (1.47 Å) bond length is greater than the other ring C–C bond lengths. The optimized geometry shows that the quinazolinone ring is planar with the $–CCl_3$ and $–CH_3$ group as evident from the dihedral angle C10–N1–C2–C11 (180˚). The calculated ring dihedral angles confirm that the ring is coplanar.

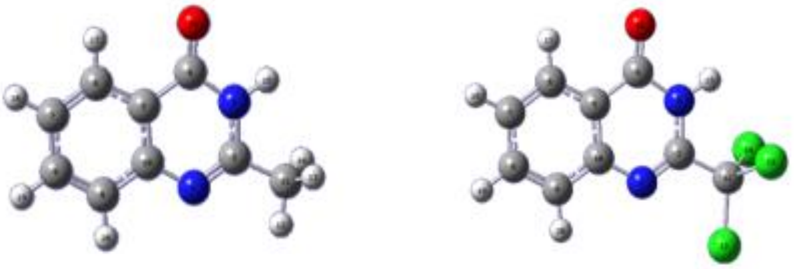

Figure 1: Optimized structure of MHQ and TCMQ

3.2 Spectral Analysis: The theoretically calculated DFT force fields are transformed in this latter set of vibrational coordinates and used in all subsequent calculations. The 54 normal modes of MHQ and TCMQ are distributed among the symmetry species as

Γ_{3N-6} = 37 A' (in-plane) + 17 A'' (out-of-plane), and in agreement with C_1 and C_s point group symmetry, respectively. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra were produced in common frequency scale and are shown in Figs. 2 and 3, respectively. The N−H stretch in MHQ and TCMQ has been reported to occur at 3420 cm^{-1} and 3340 cm^{-1} experimentally and agrees well with the theoretical value contributing 99% to the total PED. The appearance of a strong band in IR spectra of both the molecules at 1686 cm^{-1} (MHQ) and 1675 cm^{-1} (TCMQ) is due to the C=O stretch. The molecule MHQ, under consideration possesses one CH_3 group in ortho position. In MHQ, the IR peaks at 3030, 2925 and 2850 cm^{-1} is due to the CH_3 antisymmetric and symmetric stretching vibrations. The title molecule TCMQ, under consideration possesses one CCl_3 functional group. The three C–Cl_3 stretching vibrations are established in IR spectrum at 500 (symmetric stretching), 728 (in-plane stretching) and 807 cm^{-1} (out-of-plane stretching).

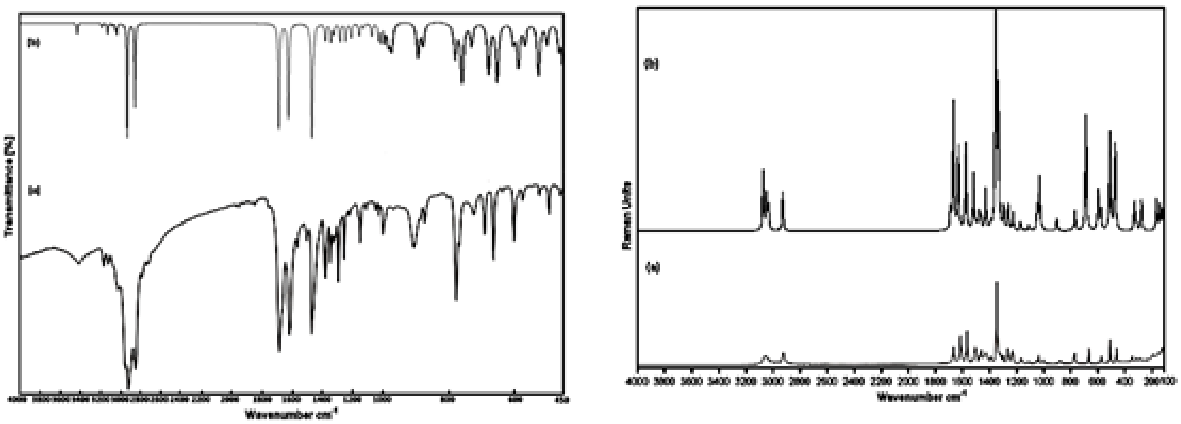

Figure 2: Comparison of (a) observed and (b) calculated FT-IR, FT-Raman Spectra of MHQ

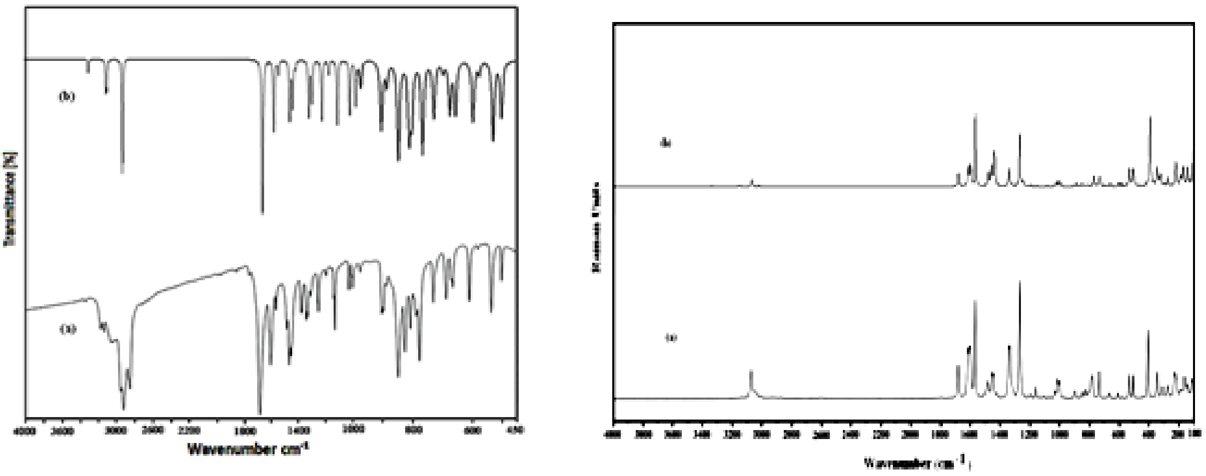

Figure 3: Comparison of (a) observed and (b) calculated FT-IR, FT-Raman Spectra of TCMQ

3.3 Hyperpolarizability: The computed value of the total static first hyperpolarizability (β_{tot}) of MHQ and TCMQ are 1.068 X 10^{-30} and 7.378 X 10^{-30} esu. From the calculated values, it is seen that TCMQ shows large NLO property. The charge delocalization is found to be maximum along β_{xxx} (MHQ) and β_{yyy} (TCMQ) components and so these directions are suitable for SHG.

3.4 NMR Analysis: The range of the ^{13}C NMR chemical shifts for a typical organic compounds usually is >100 ppm [5, 6]. In MHQ and TCMQ, the C4, C2 and C10 atoms experiences a downfield and have a high ppm value of about 161.73 (161.92), 154.24 (150.56) and 148.89 (145.89) ppm respectively. The carbons C5, C6, C7, C8 and C9 have a chemical shift value between the range 120-135 ppm in both the molecules. The C11 carbon of -CCl_3 group observes a chemical shift of about 92.53 ppm. The H15 atom observes about 12.2 (MHQ) and 13.34 (TCMQ) ppm. But a controversial part is that the predicted value is less than the observed value. This is because the theoretical value is calculated for these molecules in gas phase.

3.5 UV-Visible Analysis: Time-dependent density functional theory (TD-DFT) calculation has been performed for the chosen compounds on the basis of fully optimized ground state structure to investigate the electronic absorption properties. Both the compounds are characterized by three bands. The shorter wavelength band at 264.42 nm (MHQ) and 204.09 nm (TCMQ) is ascribed to $\pi \rightarrow \pi^*$ transition of the benzene ring system. This is common for aromatic systems like quinazolinone. The other two wavelengths 305.81 nm (MHQ), 229.30 nm (TCMQ) and 315.89 nm (MHQ), 283.20 nm (TCMQ) are ascribed to the $\pi \rightarrow \pi^*$ transition of the heterocyclic ring and $n \rightarrow \pi^*$ transition of the carbonyl fragment. A significant shift on the shorter wavelength band of TCMQ compared to MHQ might be due to the influence of the 2-substituted trichloro methyl group on the electronic transitions within the ring.

3.6 Frontier Molecular Orbitals: The HOMO-LUMO orbitals are computed at B3LYP/6-311++G** level for the title molecules and the band gap energy of MHQ and TCMQ are found to be 3.6513 and 2.2189 eV respectively. The energy gap values suggest that TCMQ is highly reactive than MHQ.

3.7 Analysis of Molecular Electrostatic Potential: The MEP mapped surfaces of both the molecules reveals that oxygen surface is highly nucleophilic while nitrogen is relatively less nucleophilic site. The hydrogen atoms constitute the electrophilic region of the molecules. The green coloured surface shows the zero potential region of the molecules.

3.8 NBO Analysis: The most significantly interacting NBOs and their second order perturbation stabilization energies $E^{(2)}$ for MHQ and TCMQ have been calculated. In MHQ, the hyper conjugative delocalization is very strong between the LP(1)N3 and the antibonding π orbitals (N1–C2) and (C4–O16) producing a stabilization energy of about 49.87 and 48.37 kcalmol^{-1}. An appreciably higher $E^{(2)}$ value has been predicted for the interactions between LP(2)O16 $\rightarrow$ σ*(N3–C4),π(C5–C10) $\rightarrow$ π*(C4–O16) and π(C8–C9) $\rightarrow$ π*(C5–C10) and are found to be 28.22, 25.85 and 20.79 kcalmol^{-1}.

4. Conclusion:

The FT-IR and FT-Raman studies of quinazolinone derivatives were carried out. The theoretically predicted FT-IR and FT-Raman spectrum shows good correlation with experimentally observed FT-IR and FT-Raman spectrum. The lower energy gap value clearly explains the charge transfer interactions taking place within the molecule which leads to its enhanced bioactivity. Predicted electronic absorption spectra from TD-DFT calculation have been analyzed by comparing it with the experimental UV-Visible spectrum and they are mainly derived from the contribution of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ band. Thus the aromaticity, equilibrium geometry, bonding features, electrostatic potential and natural atomic charges of these derivatives have been investigated.

5. References:

1. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
2. T. Sundius, J. Mol. Struct. 218 (1990) 321–326.
3. T. Sundius, Vib. Spectrosc. 29 (2002) 89–95.
4. A. Frisch, A.B. Nielson, A.J. Holder, Gauss view Users Manual, Gaussian Inc., Pittsburgh, PA, 2000.
5. H.O. Kalinowski, S. Berger, S. Brawn, Carbon 13NMR spectroscopy, John Wiley and Sons, Chichester, 1988.
6. K. Pihlajer, E. Kleinpeter (Eds.), Carbon 13Chemical shifts in structure and Spectrochemical analysis, VCH Publishers, Deerfield Beach, 1994.